Erratum: Correlations between the interfacial chemistry and current-voltage behavior of *n*-GaAs/liquid junctions [Appl. Phys. Lett. 57, 1242 (1990)]

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Correlations between the surface chemistry of etched, (100) oriented *n*-GaAs electrodes and their subsequent photoelectrochemical behavior have been probed by high-resolution x-ray photoelectron spectroscopy. GaAs photoanodes were chemically treated to prepare either an oxide-free near-stoichiometric surface, a surface enriched in zero-valent arsenic (As^0), or a substrate-oxide terminated surface. The current-voltage (*I-V*) behavior of each surface type was subsequently monitored in contact with several electrolytes.

This article is republished in its entirety due to composition errors.

The chemical nature of recombination sites at GaAs surfaces and GaAs/metal junctions has attracted attention from numerous research groups.[1–5] Models invoking the presence of interfacial defects,[3] excess elemental arsenic (As^0),[1] or metal-induced gap states[4] have been proposed to rationalize the behavior of these junctions. Our approach to this problem has been to employ GaAs/liquid contacts[6,7] to monitor changes in current-voltage (*I-V*) behavior in response to changes in interfacial chemistry. In this work, we have used *n*-GaAs electrodes exposed to chemical treatments that initially yielded either an etched interface with minimal amounts of oxides, an interface rich in As^0, or an oxide-covered surface. These studies have provided valuable correlations between junction transport behavior and GaAs surface composition.

Figure 1(a) displays the effect of various surface treatments on the photoelectrochemical *I-V* behavior of the *n*-GaAs/acetonitrile (CH_3CN)-90.0 mM ferrocene ($FeCp_2$)-0.5 mM ferrocenium hexafluorophosphate ($FeCp_2PF_6$)-0.7 M lithium perchlorate ($LiClO_4$) junction. Procedures for manipulation of these air sensitive cells and for three-electrode potentiostatic control of GaAs photoelectrodes have been described previously.[7] The initial, etched surface was prepared by exposure of the GaAs [5-μm-thick epilayer of (100) oriented, $N_d = 1.3\times10^{17}$ cm^{-3} Se-doped material on an n^+-GaAs substrate] to 1.0 M $KOH_{(aq)}$ for 30 s, followed by four repeated exposures to 0.05% (vol) Br_2-CH_3OH and then 1.0 M $KOH_{(aq)}$ solutions (15 s each); designated as etch A.[8] In the *n*-GaAs/CH_3CN-$FeCp_2^{+/0}$ cell, this surface produced an open circuit voltage (V_{oc}) of (568 ± 10) mV at a short circuit photocurrent density (J_{sc}) of 0.21 mA cm^{-2} [Fig. 1(a)]. Previous work[8] has shown that an As^0-rich GaAs surface can be obtained by etching GaAs as described above and then immersing the sample for 60 s in a 1:1:100 (vol) con. H_2SO_4:30% H_2O_2:H_2O solution; designated as etch B. No measurable difference in *I-V* properties was observed for such an As^0-rich *n*-GaAs surface in contact with the CH_3CN-$FeCp_2^{+/0}$ electrolyte [Fig. 1(a)]. In contrast, an oxide-covered surface (prepared by exposing an As^0-rich surface to stirred 30% $H_2O_{2(aq)}$ for 60 s, rinsing with H_2O, and drying with a stream of N_2; etch C)[8] yielded a V_{oc} of 425 mV at $J_{sc} = 0.09$ mA cm^{-2}, and displayed low fill factors in contact with the CH_3CN-$FeCp_2^{+/0}$ electrolyte [Fig. 1(a)].

Additional *I-V* data were obtained for these GaAs surfaces in contact with an aqueous 1.0 M KOH-0.8 M K_2Se-0.1 M K_2Se_2 electrolyte. The KOH-$Se_{(aq)}^{-/2-}$ system was chosen for study because it has been shown to provide effective kinetic competition with aqueous-based photocorrosion processes.[6] In contact with the KOH-$Se_{(aq)}^{-/2-}$ medium, *n*-GaAs surfaces exposed to all three etching treatments produced essentially identical *I-V* characteristics [Fig. 1(a)]. *n*-GaAs/Au Schottky barriers [Fig. 1(b)] showed slight differences in V_{oc} from the near-stoichiometric surface, etch A ($V_{oc} = 333$ mV at $J_{sc} = 0.20$ mA cm^{-2}), to the As^0-rich surface, etch B ($V_{oc} = 374$ mV at $J_{sc} = 0.20$ mA cm^{-2}), whereas the oxidized *n*-GaAs surface, etch C, yielded low fill factors (< 0.25) and a V_{oc} of 470 mV at $J_{sc} = 0.20$ mA cm^{-2}.

A consistent chemical interpretation of the *I-V* behavior described above can be obtained by reference to the solubility properties of Ga, As, and their oxides. The solubility of Ga oxides and As oxides in aqueous solutions of $pH > 12$ is well documented.[9] In addition, we have verified experimentally that both yellow and gray arsenic are soluble in KOH-$Se_{(aq)}^{-/2-}$ solutions, confirming previous suggestions to this effect.[10] These properties correlate well with the insensitivity of the GaAs/KOH-$Se_{(aq)}^{-/2-}$ *I-V* data to the initial condition of the GaAs surface [Fig. 1(a)]. In addition, we have verified that gallium oxide, arsenic oxide, and As^0 are insoluble in CH_3CN or in the CH_3CN-$FeCp_2^{+/0}$ electrolyte. Thus, this nonaqueous solvent sys-

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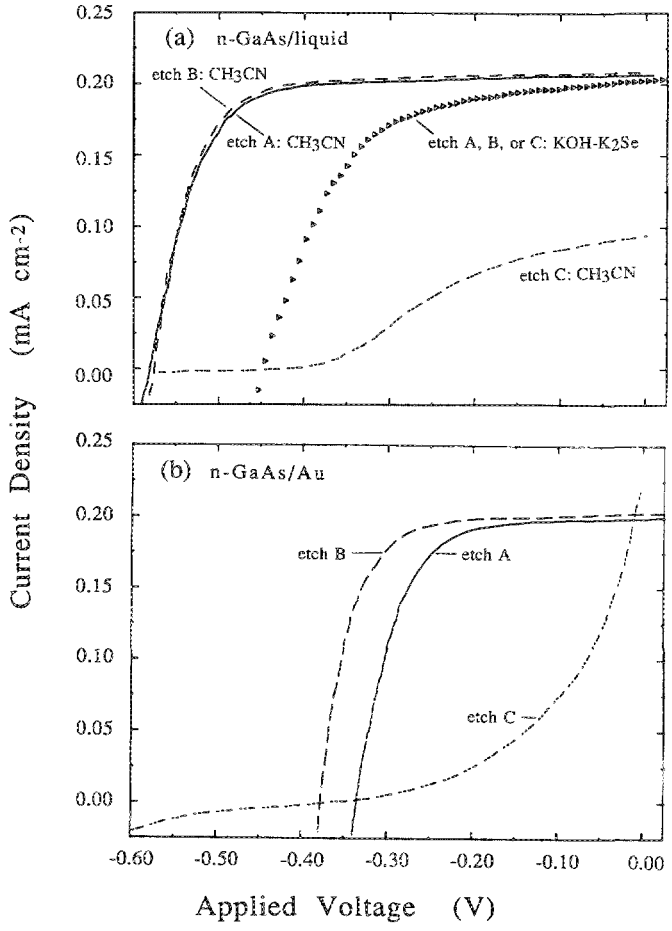

FIG. 1. (a) Potentiostatic I-V curves (50 mV/s scan rate) of various n-GaAs/liquid interfaces. (b) I-V measurements (in air) of thin (100–150 Å) Au Schottky barriers formed on n-GaAs.

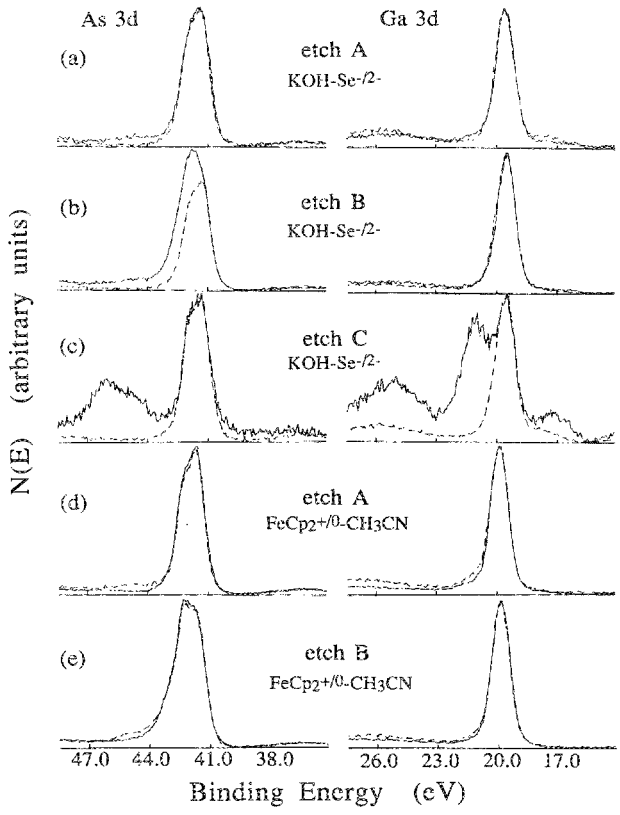

FIG. 2. X-ray photoelectron spectra of n-GaAs surfaces. In each panel, the solid line is the etched sample and the dashed line is after photoelectrochemical cycling in the indicated electrolyte. Wide scans for samples in (a)–(c) consistently displayed XPS signals only from As, Ga, O, Se, and C sources; samples (d) and (e) yielded the same surface composition except that no signal intensity was observed due to Se. None of the samples displayed signal intensity due to S, Br, K, Fe, Li, Cl, F, or P sources. For etch A, the As $3d$ doublet showed a 3:2 area ratio, indicating negligible As^0. Etch B yielded an increased coverage of As^0, as evidenced by the change in the As $3d$ doublet ratio. The excess As was removed in $KOH\text{-}Se^{-/2-}$ but remained after exposure to the $CH_3CN\text{-}FeCp_2^{+/0}$ electrolyte. For etch C, the peaks at $\approx$44, 46, and 21 eV indicated As_2O_3, As_2O_5, and Ga_2O_3, respectively, and photoemission from oxygen $2s$ core levels gave rise to the peak partially shown at $\approx$25 eV. The oxides were removed after exposure to $KOH\text{-}Se^{-/2-}$.

tem is better suited than the $KOH\text{-}Se_{(aq)}^{-/2-}$ medium for probing the dependence of n-GaAs photoelectrochemical properties on initial surface stoichiometry.

The lower V_{oc}, decreased fill factor, and the presence of an inflection point[6,10] for n-GaAs/$KOH\text{-}Se_{(aq)}^{-/2-}$ interfaces ($V_{oc} = 436$ mV; $J_{sc} = 0.20$ mA cm^{-2}) relative to the properties of etched n-GaAs in contact with $CH_3CN\text{-}FeCp_2^{+/0}$ have been previously interpreted in terms of slow hole transfer rates into the $KOH\text{-}Se_{(aq)}^{-/2-}$ electrolyte,[11,12] and our data are consistent with these conclusions. The lack of substantial differences in the n-GaAs/$CH_3CN\text{-}FeCp_2^{+/0}$ I-V characteristics for $Br_2\text{-}CH_3OH$/KOH etched (etch A) and As^0-rich (etch B) n-GaAs surfaces [Fig. 1(a)], and the relatively large values of V_{oc} for As^0-rich surfaces (etch B) in contact with $CH_3CN\text{-}FeCp_2^{+/0}$ compared to those of n-GaAs/Au contacts [Fig. 1(b)], indicates that the presence of interfacial elemental As^0 on the GaAs surface is not sufficient to induce low barrier heights and large interfacial electrical recombination currents at all n-GaAs surfaces. This is consistent with the findings of Aspnes and Stocker,[8] who observed reductions in the reverse bias dark current for As^0-rich surfaces on InGaAs mesa diodes, but is not consistent with expectations of high GaAs surface recombination rates associated with the presence of excess interfacial As.

Support for the interpretation of the GaAs/CH_3CN contact chemistry has been obtained from high-resolution x-ray photoelectron spectroscopic (XPS) analysis.[13] Figure 2 displays representative As $3d$ and Ga $3d$ XPS signals for each GaAs etch treatment before and after photoelectrochemical cycling in contact with $CH_3CN\text{-}FeCp_2^{+/0}$ or $KOH\text{-}Se_{(aq)}^{-/2-}$ electrolytes, and Table I summarizes the analysis of the various surface species found on each sample. Consistent with the solubility and I-V data, photoelectrochemical cycling of n-GaAs (0.05–3.8 C cm^{-2} of anodic charge) in contact with the $KOH\text{-}Se_{(aq)}^{-/2-}$ electrolyte resulted in identical final GaAs surface compositions after either etch A, B, or C [Figs. 2(a)–2(c), and Table I]. Regardless of the initial surface composition, extremely small residual signals for Ga or As oxide were observed, and the intensity ratios of the As $3d$ doublet peaks were consistent with that expected for substrate As, with less than 1×10^{-10} mol cm^{-2} of As^0 remaining. In contrast, after etching (etch B) the ratio of the As $3d$ doublet peaks clearly indicated the presence of As^0, and this doublet ratio

TABLE I. Surface composition of (100) *n*-GaAs electrodes.

Experiment	Surface coverage ($\times 10^9$ mole cm^{-2}) As^0	As_2O_3	Ga_2O_3
Etch A	<0.1[a]	0.5	0.2
Etch A[b] + $KOH_{(aq)}$-$Se^{-/2-}$	<0.1[a]	0.2	0.1
Etch B	2.3	0.3	<0.1
Etch B[b] + $KOH_{(aq)}$-$Se^{-/2}$	<0.1[a]	0.2	<0.1
Etch C	<0.1[a]	1.2[c]	2.4[c]
Etch C[b] + $KOH_{(aq)}$-$Se^{-/2-}$	<0.1[a]	0.1	0.1
Etch A	<0.1[a]	<0.1	0.1
Etch A[d] + $FeCp_2^{-/0}$-CH_3CN	<0.1[a]	0.3	0.5
Etch B	1.5	0.4	0.2
Etch B[d] + $FeCp_2^{+/0}$-CH_3CN	1.7	0.6	0.2

[a]No x-ray photoelectron signal intensity from As^0. X-ray excitation was obtained from a monochromatized Al K_α (1486.6 eV) small spot source.
[b]Cycling in KOH-$Se_2^{-/2-}{}_{(aq)}$ electrolyte (0.05–3.8 C cm^{-2}) stripped substrate oxides and As^0 from each surface. Weak additional XPS signals attributable to $Se_x^{(0/-2)}$ [Se 3*d* 54.4 eV, $(9\pm4)\times10^{-10}$ mole cm^{-2}] and a reduced gallium species [Ga 3*d* (18.0±0.3) eV, $(1.0\pm0.3)\times10^{-9}$ mole cm^{-2}] consistently accompanied samples cycled in KOH-$Se_{(aq)}^{-/2-}$ electrolyte.
[c]Thick oxide layer led to a range ± 20% in surface coverage.
[d]42 mC cm^{-2} anodic current in $FeCp_2^{+/0}$-CH_3CN.

did not change substantially after photoelectrochemical cycling in CH_3CN-$FeCp_2^{+/0}$ [Fig. 2(e), Table I]. This behavior in CH_3CN verifies the assertion above that the *I-V* curves in this system provide a useful probe of the electrical recombination properties of the various initial surface treatments. Notably, the XPS data confirm that the presence of excess As^0 does not necessarily lead to large recombination rates and low open circuit voltages at all GaAs interfaces, as shown by the *I-V* properties of the As^0-rich sample in contact with CH_3CN-$FeCp_2^{+/0}$ [Fig. 1(a), etch B].

The near-stoichiometric GaAs surfaces obtained in this work also yield improved photoelectrochemical efficiencies in CH_3CN compared to previous etching procedures.[7] Under 88 mW cm^{-2} of ELH-type irradiation, we have observed V_{oc} values of 0.83 V, short circuit photocurrent densities of 20.0±0.5 mA cm^{-2}, fill factors of 0.54–0.64, and efficiencies of 11.0±1.0% for mirror finished, Br_2-CH_3OH/KOH etched *n*-GaAs samples (etch A) in contact with 1.0 M $LiClO_4$-0.20 M $FeCp_2$-0.5 mM $FeCp_2^+$-CH_3CN electrolyte. These GaAs/CH_3CN V_{oc} values far exceed those reported for GaAs Schottky barrier systems,[14] and are comparable to the best values reported for any GaAs surface barrier device at these photocurrent densities.[14] The bulk recombination/diffusion limited V_{oc} for this material is approximately 1.02 V when $J_{sc} = 20$ mA cm^{-2},[14] implying that even further improvement in *I-V* properties is possible with additional control over the GaAs surface chemistry.

In conclusion, we have shown that nonaqueous photoelectrochemical methods (*I-V* experiments) may be applied to *n*-GaAs interfaces in order to assess the electrical recombination properties of various surface treatments. We have demonstrated that the presence of interfacial As^0 does not necessarily lead to large recombination rates and poor *I-V* behavior at all GaAs interfaces. Additionally, we have shown that *n*-GaAs electrodes with initially different surface compositions (etches A, B, or C) yield a common final state surface composition and *I-V* characteristic when exposed to the aqueous based KOH-$Se^{-/2-}$ electrolyte. Maintaining surface stoichiometry has led to high efficiency GaAs/liquid interfaces, but even higher V_{oc} values should be possible. Methods to achieve even better interface properties, and to minimize further the residual interfacial carrier recombination sites, are being explored at present.

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